Jan. 13, 1959 K. P. LANNEAU ET AL 2,868,986

ION RESONANCE MASS SPECTROMETER

Filed June 8, 1954

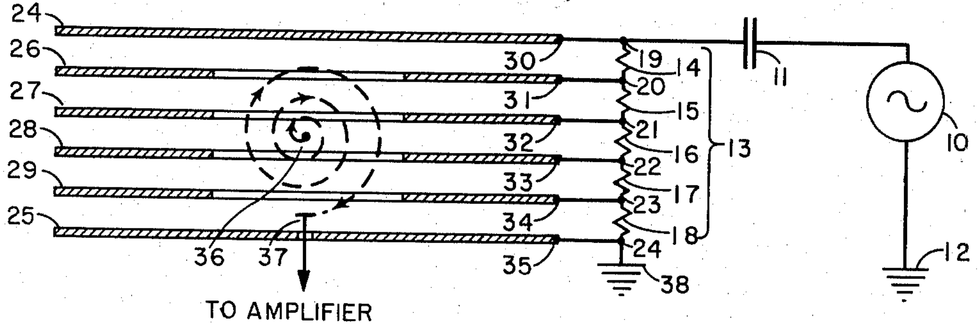

FIG. 1

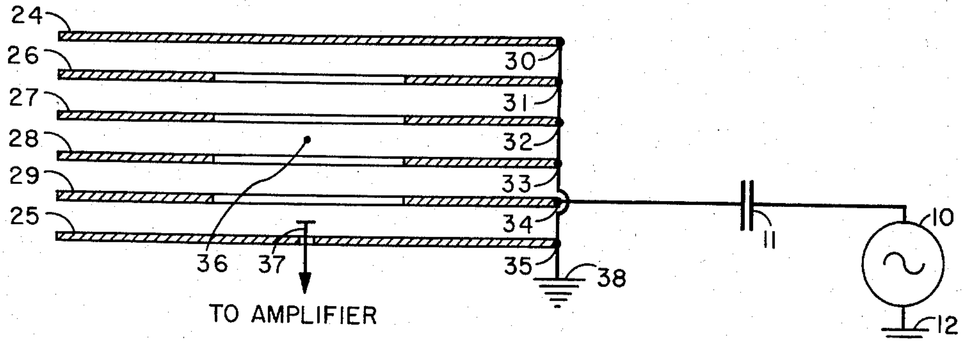

FIG. 2

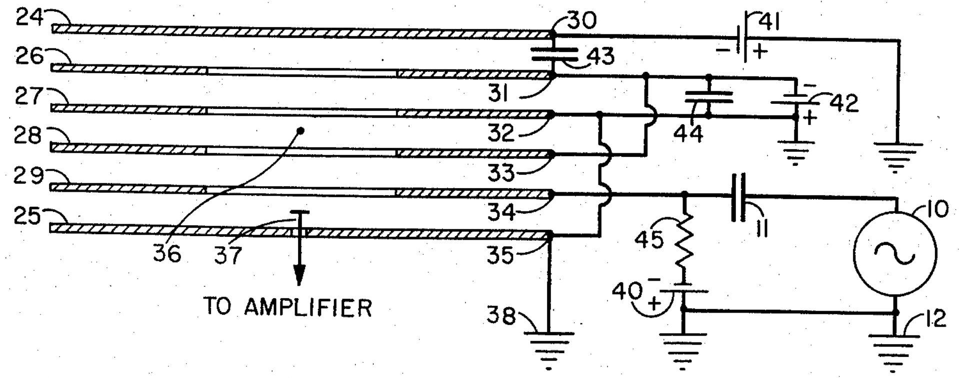

FIG. 3

KEITH P. LANNEAU
LLOYD H. LANE *INVENTORS*

BY George J. Gilbany *ATTORNEY*

United States Patent Office

2,868,986

Patented Jan. 13, 1959

2,868,986

ION RESONANCE MASS SPECTROMETER

Keith P. Lanneau and Lloyd H. Lane, Baton Rouge, La., assignors to Esso Research and Engineering Company, a corporation of Delaware

Application June 8, 1954, Serial No. 435,160

5 Claims. (Cl. 250—41.9)

This invention relates to mass spectrometry and more particularly relates to radio frequency ion resonance mass spectrometry. Still more particularly, this invention relates to a method and means for applying voltage potentials to plates of a radio frequency ion resonance mass spectrometer.

The application of mass spectrometry in the industrial field has become increasingly more important in recent years and the techniques of mass spectrometry have made possible accurate and rapid analyses of the components of gaseous mixtures. For example, mass spectrometers have been successfully utilized for continuous process monitoring, routine gas analysis, leak detection, and trace constituent analysis. One particular type of mass spectrometer is the radio frequency ion resonance mass spectrometer. This type of mass spectrometer has been described in the literature, such as in a paper presented at the American Chemical Society Symposium on Process Instrumentation, Chicago, Illinois, September 9, 1953, entitled "An Ion Resonance Mass Spectrometer for Industrial Application," by W. A. Morgan, G. Jernakoff and K. P. Lanneau. In this particular type of mass spectrometer, the gaseous sample is introduced at a low pressure into an ionization chamber wherein the gaseous molecules are ionized by means of an electron stream from a hot wire filament made from tungsten, tungsten carbide, etc. The ions formed in the ionization chamber are then accelerated in a spiral path of increasing diameter in a plane perpendicular to the electron beam. This is accomplished by a combination electric and magnetic field. In this particular type of mass spectrometer, the ionization chamber serves as the analyzer section as well as the ionization section of the mass spectrometer. The electric field is provided by means of a series of radio frequency voltage plates arranged so as to produce a linear and uniform radio frequency electric field which acts perpendicular to the electron beam. This is the design of the "Omegatron." The voltage plates are normally arranged parallel one to the other with all but the end voltage plates provided with a central opening, which opening defines the ionization chamber and the analyzer section of the mass spectrometer. The magnetic field, which may be produced by a permanent magnet or electromagnet, is aligned with the electron beam so that the magnetic field acts perpendicularly to the electrical field. A radio frequency voltage oscillator is electrically connected to one of the end voltage plates which is in turn connected to the other voltage plates through a resistance divider network. The other end voltage plate is grounded. An ion target extends partially into the analyzer section of the radio frequency ion resonance mass spectrometer and serves as a target for collecting the ions during the analysis of the gaseous sample. The impingement of the ions on the ion target produces a small ion current which is then amplified and recorded to thereby measure the amount of each ion mass formed in the ionization chamber.

By varying the frequency of the radio frequency voltage impressed on the radio frequency voltage plates, it is possible to measure the amounts of ions of different mass/charge (*m/e*) ratios. In general, for a given frequency electric field and a given strength magnetic field, only ions of one particular *m/e* will impinge upon the ion target, and these particular ions are known as resonant ions. The ion resonance principle is described in detail in the article in Physical Review of June 1, 1951, entitled "The Measurement of *e/m* by Cyclotron Resonance" by H. Sommer, H. A. Thomas and J. A. Hipple. More specifically only the ions formed in the ionization chamber which are resonant will continue to be accelerated in a spiral path of increasing diameter so as to impinge upon the ion target. The non-resonant ions, on the other hand, will oscillate in the analyzer section due to the effect of the electrical and magnetic fields but will never be accelerated sufficiently to impinge upon the ion target. These non-resonant ions periodically spiral to a maximum radius or distance short of the ion target and then spiral back to the center of the analyzer section or tube as this section is sometimes called. It is essential that both a radio frequency (R. F.) electric field and a magnetic field be employed in this type of mass spectrometer in order to accomplish these results.

Features such as resolving power, sensitivity, linearity, cracking stability, background interference, etc., are important in analytical mass spectrometers. In particular, the present invention is concerned with the resolving power, sensitivity, stability and linearity of ion resonance mass spectrometers or Omegatrons. The resolving power of a mass spectrometer is a measure of its ability to separate ions of a particular *m/e* ratio from ions of other *m/e* ratios. The sensitivity of a mass spectrometer is a measure of its ability to collect on the ion target a high concentration of ions of a particular *m/e* ratio and to reject others. Linearity is a measure of the ability of a mass spectrometer to produce an ion current whose magnitude is directly proportional to the concentration of resonant ions which are formed by the electron bombardment of sample gas molecules. For an analytical instrument it is further required that ions of a given *m/e* ratio be formed in direct proportion to the molecular concentration of each constituent in the sample. Also for analytical instruments it is important that the overall sensitivity and cracking stability be virtually constant.

The present invention provides a method and means for improving these qualities of a radio frequency ion resonance mass spectrometer. This is accomplished by employing a particular non-linear and asymmetrical R. F. field rather than the linear R. F. fields now employed in these types of mass spectrometers wherein the amplitude of the radio frequency voltage varies linearly from voltage plate to voltage plate. A substantial improvement in the resolving power, sensitivity, stability and linearity of an ion resonance mass spectrometer is effected by the present invention. In addition, the present invention is concerned with the application of direct current voltages to the voltage plates in combination with the radio frequency voltage impressed on the plates. The present invention also concerns the combination of a non-linear asymmetric R. F. electric field and the utilization of specific D. C. voltages in an ion resonance mass spectrometer. The application of these D. C. voltage potentials in combination with the conventional linear R. F. field or with the non-linear asymmetrical R. F. electric field of this invention, results in a substantial improvement in the resolving power, sensitivity, stability and linearity of the radio frequency ion resonance mass spectrometer.

The discussion regarding the present invention will be apparent from a reading of the specification, which may be more clearly understood by reference to the drawings in which:

Fig. 1 is a diagrammatic cross-sectional view of a conventional radio frequency ion resonance mass spectrometer, taken perpendicular to the electron beam;

Fig. 2 is a diagrammatic cross-sectional view of a radio frequency ion resonance mass spectrometer showing a particular embodiment of the present invention for producing a non-linear asymmetrical electric field, and

Fig. 3 is a diagrammatic cross-sectional view of a radio frequency ion resonance mass spectrometer, similar to Fig. 2, showing another embodiment of the present invention which incorporates a combination of a non-linear radio frequency electric field and a D. C. voltage field.

Referring now to the drawings, Fig. 1 illustrates a conventional radio frequency ion resonance mass spectrometer. The mass spectrometer is provided with oscillator **10** for producing an R. F. electric field. Oscillator **10** is connected to ground **12** and to plate **24** through coupling condenser **11**. Reference character **13** designates a resistance divider network which comprises a series of equal resistances **14**, **15**, **16**, **17**, and **18**. Divider network **13** is provided with electric taps **19**, **20**, **21**, **22**, **23**, and **24** for connection to the radio frequency voltage plates of the mass spectrometer. The mass spectrometer is provided with end voltage plates **24** and **25** and a series of voltage grading plates **26**, **27**, **28**, and **29** which are provided with central openings so as to provide a zone for the analyzing section of the mass spectrometer. The voltage plates are provided with electric taps **30**, **31**, **32**, **33**, **34**, and **35** for electrical connection to the electric taps of divider network **13**. Thus, electric tap **30** is connected to electric tap **19**; electric tap **31** is connected to electric tap **20**; electric tap **32** is connected to electric tap **21**; electric tap **33** is connected to electric tap **22**; electric tap **34** is connected to electric tap **23**, and electric tap **35** is connected to electric tap **24**. In this particular arrangement, the R. F. electric field is linearly distributed from plate **24** to voltage plate **25** through grading plates **26** to **29**. This results in a linear and uniform R. F. field in a region enclosed between the end plates and cutouts of the intermediate plates.

Electron beam **36** is directed perpendicularly to the plane of Fig. 1 and through the center of the ionization chamber which, in this type of mass spectrometer, also serves as the analyzer section of the mass spectrometer. The resonant ions follow the spiral path indicated by the dotted lines in the analyzer section of the mass spectrometer and impinge upon ion target **37**. The ion current produced by the impingement of the resonant ions on ion target **37** is generally sent to an ion current amplifier and then to a recording device. Divider network **13** and voltage plate **25** are connected to ground **38**. The foregoing, as illustrated in Fig. 1, is conventional in radio frequency ion resonance mass spectrometers.

Fig. 2 illustrates an embodiment of the present invention which utilizes a non-linear asymmetrical R. F. electric field; that is asymmetrical as related to the center of the tube. In this particular form of the present invention, oscillator **10** which is employed to produce an R. F. electrical voltage is connected to ground **12** and electric contact **34** of voltage grading plate **29** through coupling condenser **11**. Voltage plates **24** and **25** and grading plates **26**, **27**, and **28** are connected by means of electric taps **30**, **35**, **31**, **32**, and **33**, respectively, to ground **38**, such that all voltage plates except voltage grading plate **29** are at ground potential. Thus only voltage grading plate **29** is coupled by circuit component to the R. F. voltage produced by oscillator **10**. Although the action of the non-linear electrical field on the ions which are formed by electron beam **36** and which are directed to ion target **37** is not fully understood, the result of the present invention is to substantially increase the resolving power, sensitivity, linearity and stability of the mass spectrometer. It will be noted that the divider network **13** shown in Fig. 1 is not utilized in the form of invention shown in Fig. 2.

It is to be clearly understood that the R. F. electric voltage may be impressed on any one of the voltage grading plates **26**, **27**, **28**, or **29** and is not restricted solely to voltage grading plate **29**. It will also be understood that the form of the present invention illustrated in Fig. 2 is not restricted to four voltage grading plates as shown but may be employed with more or less voltage grading plates in accordance with the present invention. It is preferred however to couple the R. F. voltage from oscillator **10** through a circuit component to one of the plates near or adjacent to the end plate through which the ion target is inserted. It will further be understood that other means for developing non-linear asymmetrical fields can be utilized in this invention.

Referring now to Fig. 3, it will be seen that the non-linear electric field shown in Fig. 2 is combined with a unique application of D. C. voltage to the plates. Oscillator **10** is employed to produce a radio frequency voltage and is connected to ground **12** and electrical tap **34** of voltage grading plate **29** through coupling condenser **11** in the same way as in Fig. 2.

It will be noted that the circuit shown provides for essentially the same R. F. fields developed by the circuit of Fig. 2. In this case capacitors **43** and **44** are of sufficient magnitude to provide a virtual short circuit for R. F. voltages of the frequencies with which we are concerned. Therefore, as in Fig. 2, the R. F. voltage is supplied from the oscillator **10** to plate **29** through capacitor **11** and tap **34**, and all other plate elements are at essentially "R. F. ground potential."

Fig. 3 differs from Fig. 2 only in the respect that certain D. C. voltages have been applied in combination with the same R. F. circuit.

Voltage sources **40**, **41**, and **42** may be variable sources of D. C. potential in the range of 0.001–3 volts such as would be derived from batteries and low resistance divider networks. These voltage sources have a common positive side, which is at ground potential. The negative side of D. C. voltage source **41** is applied to plate **24** at tap **30** and is isolated from the other plates by capacitor **43**. The negative side of D. C. voltage source **42** is applied to grading plates **26** and **28** at taps **31** and **33** respectively. Capacitor **44** serves as an R. F. short to ground across D. C. voltage source **42**. Plates **27** and **25** are directly connected to ground.

As previously mentioned R. F. oscillator **10** is coupled to plate **29** at tap **34** through capacitor **11**. Also the negative side of D. C. voltage source **40** is coupled to plate **29** at tap **34** through resistor **45**. Resistor **45** is of sufficient magnitude to prevent impedance loading of oscillator **10**.

If R. F. potential is applied to a plate other than **29**, then D. C. voltage source **40** may also be applied to the same plate as the R. F. It is preferable however that this plate be near target **37**. D. C. source **41** is preferably applied to terminal plate **24** in any case. D. C. voltage source **42** might be applied to a pair of plates other than **26** and **28**, but in any case such pair of plates should be in the central part of the tube and should lie on either side of a grading plate near the center of the tube and the electron beam.

It is essential that the polarity of the D. C. voltages developed by D. C. sources **40**, **41**, and **42** be as indicated in Fig. 3. The magnitudes of the three potentials developed by these batteries are simultaneously adjusted to give optimum sensitivity, linearity and resolution for the mass spectrometer. This will also result in the best stability. For different *m/e* ratios, R. F. voltages, electron beam intensities, and operating pressures, there may be different optimum values for the D. C. voltages, but it is possible to select an optimum set of D. C. voltages which produce excellent results over an extended range in the mass spectrometer. It will be understood that the application of D. C. voltages to the R. F. voltage field may be employed with a linear R. F. voltage field or any form of non-linear asymmetrical R. F. voltage field with desirable results.

A comparison was made on operating characteristics of (I) a linear R. F. field ion resonance mass spectrometer substantially as shown in Fig. 1 with (II) the ion mass spectrometer of this invention utilizing a non-linear asymmetrical R. F. field substantially as shown in Fig. 3. In both cases optimum D. C. potentials were applied to the plates. The results are as follows:

Results	I Linear R. F. Field	II Non-Linear R. F. Field	
Maximum ion mass (m/e) satisfactorily resolved	43	100	
Ion current magnitude at n-C_4H_{10} Mass 43 Peak, Amp	10^{-12}	10^{-10}	
Stability	Fair	Good	
	Synthesis		
Typical Analysis:	*Percent*	*Percent*	*Percent*
C_2H_6	25.0	27.0	25.4
C_3H_8	25.0	24.6	24.9
I-C_4H_8	25.0	23.8	24.2
N-C_4H_{10}	25.0	24.6	25.5

In each case various operating parameters of the tube were adjusted to provide maximum reproducibility and linearity.

These results show a decided advantage for II in terms of resolution, ion current sensitivity, stability and accuracy in a hydrocarbon gas analysis. It was found that a failure to use the D. C. voltage gives vastly inferior results in both cases.

The advantage of the asymmetrical non-linear field is believed to be due to the minimization of the space charge limitations in the operation of the tube. The D. C. potentials have a similar effect and therefore optimize focusing of the resonant ion beams. It will be understood that other non-linear types of fields may also be employed to obtain desirable results in accordance with this invention.

What is claimed is:

1. A mass analyzing instrument including an analyzer chamber, means for ionizing samples of matter introduced into said chamber, means for producing a magnetic field across said analyzer chamber, means for producing a concentrated alternating electric field gradient normal to said magnetic field across substantially only an asymmetrically disposed elemental region of said analyzer chamber, said alternating electric field having a frequency of alternation corresponding to the natural frequency of ions possessing a certain mass whereby such ions may be accelerated in spiral paths, means for collecting the ions thus accelerated, and means for removing ions having an undesired natural frequency from the region of said crossed magnetic and alternating electric fields.

2. In an ion resonance mass spectrometer, including an analyzer chamber, means for ionizing matter introduced into said chamber, whereby said matter is ionized to produce ions of characteristic mass/charge ratios, and target means in said chamber for collecting selected ions of a particular mass/charge ratio, an improved means for accelerating said ions in a spiral path whereby said selected ions substantially are accelerated in said spiral path into contact with said target means therefor, and non-selected ions substantially are removed from said spiral path and analyzer chamber, comprising in combination, means for producing a magnetic field across said chamber, means for producing a non-linear, radio frequency electric field across said chamber which field is normal to said magnetic field, asymmetrically related to the center of said chamber and of a radio frequency at which said selected ions substantially are resonant, and said non-selected ions substantially are non-resonant, and means for substantially removing said non-selected, non-resonant ions from said chamber.

3. An apparatus according to claim 2, wherein said improved means for accelerating said ions of characteristic mass/charge ratio in a spiral path includes a series of spaced, parallel voltage plates positioned within said analyzer chamber, said series comprising a pair of terminal end voltage plates and a plurality of grading voltage plates intermediate said end plates, a radio frequency voltage source including two terminals of which one is connected to ground, electrical coupling means connected between the other terminal of said radio frequency source and an intermediate grading voltage plate disposed asymmetrically of said series whereby to establish said asymmetrical, non-linear radio frequency field, and grounding means connected to the remaining voltage plates in said series.

4. In an ion resonance mass spectrometer, including an analyzer chamber, means for ionizing matter introduced into said chamber, whereby said matter is ionized to produce ions of characteristic mass/charge ratios, and target means extended into said chamber for collecting selected ions of a particular mass/charge ratio, an improved means for accelerating said ions in a spiral path whereby said selected ions substantially are accelerated in said spiral path into preferential contact with said target means therefor, and non-selected ions substantially are removed from said spiral path and analyzer chamber, comprising in combination, means for producing a magnetic field across said chamber, a series of spaced, parallel voltage plates positioned within said analyzer chamber, said series comprising a pair of terminal end voltage plates and a plurality of grading voltage plates intermediate said end plates, wherein said ion target extends into said chamber through one of said end plates, a radio frequency voltage source including two terminals of which one is connected to ground, an electrical coupling means connected between the other terminal of said radio frequency source and a grading plate disposed asymmetrically of said series and in an elemental region of said chamber which includes said ion target, whereby to establish in said region a radio frequency electrical field asymmetrically of said chamber, and which field is normal to said magnetic field and of a frequency at which said selected ions substantially are resonant, and said non-selected ions substantially are non-resonant, and means for substantially removing said non-selected, non-resonant ions from said chamber.

5. In an ion resonance mass spectrometer, including an analyzer chamber, an electron source in said chamber for ionizing matter introduced into said chamber, whereby said matter is acted upon by electrons from said source to produce ions of characteristic mass/charge ratios, an ion target in said chamber adapted to collect selected ions of a particular mass/charge ratio, an improved means for accelerating said ions in a spiral path whereby said selected ions substantially are accelerated in said spiral path into preferential contact with said ion target and said non-selected ions substantially are removed from said spiral path, comprising in combination, means for producing a magnetic field across said chamber, a series of spaced, parallel voltage plates positioned within said chamber, a radio frequency voltage source including two terminals of which one is connected to ground, electrical coupling means connected between the other terminal of said radio frequency voltage source and a first voltage plate intermediate the terminal end plates of said series and asymmetrically thereof, whereby to establish an asymmetrical, non-linear radio frequency field normal to said magnetic field, a first source of D. C. voltage, electrical coupling

means connected between the negative terminal of said first D. C. source and said first voltage plate, a second source of D. C. voltage, electrical coupling means connected between the negative terminal of said second D. C. source and a pair of voltage plates intermediate the ends of said series, said pair of voltage plates separated one from the other by a fourth intermediate plate of said series in a central portion of said chamber and said series of voltage plates, a third source of D. C. voltage, electrical coupling means connected between

the negative terminal of said third D. C. source and the terminal end plate of said series farthest removed from said ion target, and grounding means connected to the remaining voltage plates in said series which are not connected to the negative terminal of any of said voltage sources.

References Cited in the file of this patent

UNITED STATES PATENTS

2,698,389	Jernakoff	Dec. 28, 1954